

Persistence and Degradation of Pesticides in Composting

Introduction

Composting is a process in which *microorganisms* rapidly consume organic matter, using it as an energy source and converting it into carbon dioxide, water, *microbial biomass*, heat and *compost*. *Feedstock* used to fuel the composting process may originate from a number of different sources, including yard trimmings, manure, biosolids, and agricultural residues. These materials may contain a number of synthetic organic compounds or *xenobiotics*, including *pesticides*.

Many different physical and chemical factors help determine the overall *persistence* of a pesticide. In general, composting provides an optimal environment for pesticide destruction. This publication discusses the potential for a pesticide to become *inactivated* and degraded during composting.

The Composting Process

Compost is well-suited for pesticide degradation because:

- The elevated or *thermophilic* temperatures achieved during composting permit faster biochemical reactions than possible under ambient temperatures, accelerating pesticide degradation. The high temperatures can also make pesticides more *bioavailable*, increasing the chance of microbial degradation.
- Some microorganisms may co-metabolize pesticides, where the microbes rely on the feedstock for food and energy while breaking down an adjacent pesticide. Co-metabolism means that the microorganism does not receive any energy or potential food from the secondary reaction (in this case, from breaking down the pesticide). The many different organic matter *structures* in compost help to promote co-metabolism of numerous

objectionable compounds, even *recalcitrant* xenobiotics such as *DDT*, *PCB* and *TCE*.

- Compost feedstock contains numerous and diverse *active* microorganisms, all with their own characteristics and capabilities. This diversity means a greater chance that a pesticide will encounter a microbe that can degrade it.

Mechanisms Affecting Pesticides During Composting

During composting, a pesticide may undergo the following physical and/or biological changes:

Biological Degradation

Microorganisms have developed many *enzymes* that can break down natural compounds. Modern scientists, though, have created pesticides with chemical structures not found in nature. These unique structures are often responsible for a pesticide's effectiveness and also explain why pesticides can persist in the environment.

A pesticide's environmental persistence largely depends on its chemical structure and on the presence of unusual *functional groups*, which are large sub-structures within the pesticide molecule. The chemical structure helps determine its *water solubility* and consequently, its bioavailability, since microbes more readily assimilate water-soluble compounds.

When a pesticide's functional groups are attached with weak or *labile* bonds, it can degrade more rapidly. Many modern pesticides have such bonds designed into them to avoid problems of extended persistence. Adding water may break many labile bonds. This process is called *hydrolysis* and the enzymes that promote hydrolysis are termed hydrolytic. Malathion is an example of an insecticide containing many such labile bonds that may be broken using hydrolytic enzymes (for example, esterase and phosphatase).

Other pesticides capable of hydrolytic degradation are: carbamate pesticides, urea derivatives, pyrethroids, diazinon, dicamba, dichloropicolinic acid, dimethoate, phenylalkanoic ester, dimethoate, phenylalkanoic pyrazon, atrazine, linuron, propanil, chlorpyrifos, and 2,4-D. Two other classes of enzymes, mono- and di-oxygenases, are also commonly associated with pesticide degradation. These enzymes introduce one or two oxygen atoms, respectively, into the structure of a pesticide. This *oxidation* process often makes the pesticide more amenable to further degradation by increasing its water solubility, thereby increasing its bioavailability. Degradation may begin at the extracellular level and then proceed further at the intracellular level.

Extracellular Decomposition

Many of the same enzymes microorganisms use to break down cellulose, hemicellulose, and lignin—the primary natural compounds in most plant material—may also degrade pesticides during composting. The large *polymeric* structure of these natural compounds prevents their passage into the microorganism for consumption.

To deal with this problem, microorganisms begin breaking down chemicals outside their “body,” or extracellularly. They excrete enzymes out of their cells that react with the bonds in cellulose, hemicellulose, and/or lignin, breaking them down into smaller components. The shortened polymers can then be subjected to further degradation.

Extracellular enzymes can have very low “specificity,” working like a key that fits different locks. They can, therefore, react with many different chemicals. If the enzyme finds a pesticide before reaching its “intended” substrate (for example, cellulose, hemicellulose, lignin), it may react with it, changing the pesticide into a possibly less toxic and less hazardous form. Such co-metabolism appears to play a significant role in degrading pesticides found in compost and soil.

Fungi are the source of most extracellular enzymes. Some fungi often associated with compost and soil organic matter are in the genera *Trichoderma*, *Gliocladium*, *Penicillium*, and *Phanerochaete*. Fungi grow through the development of hyphae (long strings of cells) that extend throughout compost or soil organic matter.

The hyphae release extracellular enzymes, which break down the pesticide and allow it to pass into the cells. This allows the production of additional hyphae and/or energy. Although fungi are present in compost feedstock, they contribute more to composting in its later stages. As bacteria exhaust the easily degraded organic matter from the feedstock, fungi then begin to degrade the more recalcitrant polymeric organic matter.

Intracellular Decomposition

After extracellular enzymes begin breaking down a pesticide or if it is otherwise bioavailable, a pesticide may enter the cell of a microorganism. To pass into a cell efficiently, the pesticide must be dissolved in water. Generally pesticides containing more oxygen, nitrogen, and sulfur tend to be more water soluble due to *hydrogen bonding*.

Once inside a cell, a pesticide may undergo varying degrees of degradation. *Mineralization* reduces the pesticide to carbon dioxide, water, and other inorganic components. Typically, it accounts for only a small portion of the “disappearance” of a pesticide through composting.

Adsorption

Water-insoluble pesticides tend to *adsorb* onto and within organic matter, making them even less bioavailable. The chemistry of the functional groups in the pesticide and the organic matter dictates the strength of this pesticide-organic matter interaction.

Adsorbed pesticides are generally much more resistant to breakdown than water-soluble pesticides. This is because the latter have a much greater chance of contact with pesticide-degrading microorganisms as described above. Consequently, highly adsorbed pesticides are not considered bioavailable, enabling them to persist for months or even years. However, when a pesticide is adsorbed to organic matter that eventually decomposes, it may once again become bioavailable.

Additional factors can make adsorption a likely outcome for even water-soluble pesticides. For example, many pesticides contain acidic and nitrogen-containing functional groups that can adsorb due to the presence of a negative or

positive charge, respectively. A negatively charged pesticide will adsorb to positively charged functional groups on organic matter, while positively charged pesticides will adsorb to negatively charged functional groups on organic matter and clays.

Volatilization

Volatilization occurs when a pesticide *partitions* from the solid or *aqueous phase* to the gas phase. Once volatilized, a pesticide may *diffuse* into the atmosphere and either be destroyed or continue as an environmental risk. When mixing disturbs a soil contaminated by a pesticide or other organic compound, a 30 percent or greater loss of the soil contaminant through volatilization is not unusual.

Volatilization of a pesticide is highly temperature dependent; thermophilic temperatures typically increase pesticide losses. The tendency for a pesticide to volatilize also depends upon its size, structure, and function. Moisture also affects volatilization rates. Water may physically impede the flow of a gas phase pesticide by obstructing the *pores* through which gases travel. Water may also promote volatilization by liberating weakly adsorbed pesticides.

Leaching

Water-soluble pesticides have a tendency to be “rinsed away” through a process called leaching, that is, the movement of a chemical within percolating water. Typically, leaching is of concern when the pesticide moves into groundwater or another location, posing an increased risk to humans and/or the environment. Many pesticides are not highly soluble in water, readily adsorbing onto the organic matter fraction. For this reason, use of composts in agricultural soils tends to reduce the threat of pesticide leaching losses.

Case Studies

Many studies have been conducted on the fate of pesticides during composting, some of which are summarized in an article in the Winter 2000 issue of *Compost Science and Utilization*. During composting, pesticides will probably behave differently than they do when in soil. This is because of increased temperature, microbial diversity, microbial activity, and organic matter during composting. While many of these studies showed a significant reduction in detectable pesticides, they also showed only a small

percentage of pesticide is typically lost to mineralization.

Besides mineralization, the “disappearance” of pesticides may occur by volatilization, adsorption, leaching, or other methods noted earlier. A pesticide adsorbed to a compost molecule, while technically present, may also be inactivated and could permanently lose its pest control function. Many of the studies showed that concentrations of organophosphate and carbamate pesticides were lower after composting. However, recalcitrant organochlorine insecticides (for example, DDT) and pyridine carboxylic acid herbicides (for example, *clopyralid* and *picloram*) are more resistant to degradation.

Lemmon and Pylypiw (1992) studied the persistence of chlorpyrifos, diazinon, isofenphos, and pendimethalin after composting with grass clippings. The authors found the pesticides undetectable shortly after application, and they disappeared quickly after composting. Vandervoort et al. (1997) showed a similar result: decreasing concentrations of chlorpyrifos, 2,4-D, isoxaben, triclopyr, clopyralid, and fluprimsol after composting with grass clippings. Pesticide levels were below the routine detection limit after 128 days. They were typically lower in samples from inside of compost piles that had been turned versus the exterior and static piles.

Muller and Korte (1975 and 1976) found that only 12 percent of the initial aldrin, 3 percent of the dieldrin, and less than 15 percent of monolinuron and imugan added to municipal solid waste and biosolids feedstock were degraded after composting. In contrast, 55 percent of the herbicides buturon and heptachlor were degraded. Without any evidence for pesticide mineralization, the authors concluded that composting might not be suitable for treating feedstock contaminated with these persistent pesticides. Critics of this study think the three-week period too short to evaluate the potential for removal of persistent pesticides.

Racke and Frink (1989) also presented data on the limited mineralization of a pesticide during composting. Approximately 97 percent of the insecticide carbaryl was transformed during composting of municipal biosolids, but only 5 percent of this could be attributed to

mineralization. Racke and Frink ended their experiment after a short time (20 days), also drawing criticism. But both studies suggest that appreciable mineralization of a pesticide during composting may take more processing time.

Other studies focused on volatilization and mineralization in pesticide degradation. Petruska et al. (1985) showed the importance of volatilization in the remediation of pesticide-contaminated compost. Losses due to volatilization reached 22 percent for diazinon and 50 percent for chlordane after three weeks of cow manure and sawdust composting. Chlordane was not substantially mineralized, and diazinon was considerably transformed, but again with a low rate of mineralization.

Rao et al. (1995) also found minimal mineralization of the herbicide atrazine during composting with several different wood-derived substrates. After 160 days of composting, there was no detectable atrazine, yet a maximum of 7 percent had been mineralized. The unmineralized atrazine apparently leached or complexed with the humic components, preventing further *transformation*.

While many of the studies have shown significant decreases in detectable pesticides after composting, some of the pesticides were not completely degraded or mineralized. Instead, some were transformed to other chemical compounds, volatilized, adsorbed to the humic fraction, or leached out of the compost. The issue of pesticide toxicity after these types of changes is complex and varies significantly among pesticides. Some pesticides may increase in toxicity once changed, while others may be inactivated. Additional studies are necessary to better understand the fate of pesticides during composting.

Possible Precautionary Measures

Consumers and composters should note the possibility that persistent pesticides can endure the composting process at damaging levels. For example, as little as 10 parts per billion of clopyralid can be toxic to legumes, potatoes, sunflowers and tomatoes.

Clopyralid and picloram are of concern because they have shown up in compost on at least two

occasions. In particular, after the inadvertent composting of contaminated grassy material or manure at two separate Washington composting facilities, routine laboratory tests on the resulting compost by the commercial composting facility did not indicate the presence of pesticides.

Subsequent tomato damage first surfaced during 2000 and prompted more sensitive laboratory analysis of the compost that indicated 31–75 parts per billion of clopyralid. Extensive testing of materials used to make the compost identified clopyralid contaminated lawn clippings from Spokane. Later that year another herbicide-laced compost was attributed to picloram contaminated bedding and manure in Pullman. At the same location clopyralid contaminated hay and straw purchased for animal feed, and the resulting manure was also composted during 2001.

Clopyralid is apparently more problematic than picloram since the different registered uses of the two pesticides suggest that materials typically coming into a composting facility are less likely to be contaminated with picloram. As a minimum precaution, operators should become familiar with the supplier and source of each material and inquire regarding persistent herbicide usage.

Bioassays by facility operators or highly sensitive analytical tests may be advisable on incoming materials and outgoing products. Washington State University staff offers bioassay guidelines and color images of clopyralid-damaged plants at <http://css.wsu.edu/compost/bioassay.htm>.

Growers and landscapers concerned about pesticide or herbicide residues may also wish to take one or more precautionary measures before applying compost. A few herbicides are phytotoxic below detectable analytical levels, so the above bioassay guidelines may help assess the safety of a compost pile.

A simple seed germination test will ensure that a split-sample of compost is mature and any salts present are not phytotoxic. The following Florida Web site includes guidelines for conducting seed germination tests: www.compostinfo.com/tutorial/MaturityTests.htm. If either bioassay results in no germination or the young plants show symptoms of herbicide damage, it is advisable to perform analytical tests on the remainder of the sample that include tests for suspected herbicides

(parts per billion sensitivity), salinity, and compost maturity. Users also can apply the compost in a small test plot before covering an entire garden or farm.

Bibliography

Buyuksonmez, F., et al. "Occurrence, Degradation and Fate of Pesticides During Composting. Part II: Occurrence and Fate of Pesticides in Compost and Composting Systems." *Compost Science & Utilization*, Vol. 8, No. 1, Winter 2000, pp. 61–81.

Bezdicek, D., et al. "Persistent Herbicides in Compost." *BioCycle*, Vol. 42, No. 7, July 2001, pp. 25–30.

Lemmon, C. R., and H. M. Pylypiw, Jr. "Degradation of Diazinon, Chlorpyrifos, Isofenphos, and Pendimethalin in Grass and Compost." *Bulletin of Environmental Contamination and Toxicology*, Vol. 48, No. 3, March 1992, pp. 409–415.

Muller, W. P., and F. Korte. "Microbial Degradation of Benzo-(a)-pyrene, Monolinuron, and Dieldrin in Waste Composting." *Chemosphere*, Vol. 4, No. 3, 1975, pp. 195–198.

Muller, W.P., and F. Korte. "Ecological Chemical Evaluation of Waste Treatment Procedures." In F. Coulston and F. Korte (eds.), *Environmental Quality and Safety: Global Aspects of Chemistry, Toxicology and Technology as Applied to the Environment*. New York: Academic Press, 1976, pp. 215–236.

Petruska, J., et al. "A Benchtop System for Evaluation of Pesticide Disposal by Composting." *Nuclear and Chemical Waste Management*, Vol. 5, No. 3, 1985, pp. 177–182.

Racke, K. D., and C. R. Frink. "Fate of Organic Contaminants During Sewage Sludge Composting." *Bulletin of Environmental Contamination and Toxicology*, Vol. 42, No. 4, April 1989, pp. 533.

Rao, N., et al. "Mineralization of Atrazine During Composting with Untreated and Retreated Lignocellulosic Substrates." *Compost Science and Utilization*, Vol. 3, No. 3, Summer 1997, pp. 38–46.

Vandervoort, C., et al. "Fate of Selected Pesticides Applied to Turfgrass: Effects of Composting on Residues." *Bulletin of Environmental Contamination and Toxicology*, Vol. 58, No. 1, January 1997, pp. 38–45.

Glossary

Active—Having the desired effect on the desired organism. An active herbicide is one that is lethal to the plant it was intended to kill.

Adsorb (adsorption)—The association and binding of chemicals to the surface of solid particles such as soil particles and organic matter.

Aqueous phase—Located in the water phase as opposed to the solid or vapor/gas phases.

Bioavailable—Accessibility of a chemical to one or many organisms including plants, animals, and microorganisms, enabling its degradation.

Clopyralid—The active ingredient in several herbicide products registered for use on lawns, some crops or pasture (for example, Confront, Curtail, Millenium, Stinger and Transline).

Compost—A mixture of degradable and recalcitrant organic matter remaining after aerobic, thermophilic microbial decomposition and curing.

Curing—The final, mesophilic stage of composting, following the thermophilic stage, where the more recalcitrant organic matter is consumed.

DDT—One of the world's most widely used pesticides. Banned in the United States and many other industrialized countries since the 1970s.

Diffuse—To move away from a source, such as tannins from a tea bag in water and smoke from a cigarette in the air.

Enzyme—Commonly a protein that speeds up a chemical reaction or reactions.

Feedstock—Starting materials to be composted.

Functional group—One or more atoms that are bound to a larger chemical.

Hydrogen bonding—Interaction between hydrogen atoms of one chemical and the oxygen, nitrogen, or sulfur of another chemical. This interaction forms a common chemical bond called a hydrogen bond. This is commonly found in all of nature, such as between water molecules and within DNA.

Hydrolysis—The process of breaking weak chemical bonds through the addition of water, usually involving hydrolytic enzymes.

Inactivated—Temporary or permanent loss of a pesticide's activity.

Labile—Easily degraded.

Mesophilic—Temperature range of 50–105°F.

Microbial biomass—The microbiological component of soil.

Microorganisms—Diverse groups of microscopic organisms including bacteria, fungi, viruses, protozoa and algae.

Mineralization—Breakdown of an organic compound into carbon dioxide, water, and other inorganic components.

Oxidation—Introduction of one or more oxygen atoms into the structure of a chemical.

Partition—Movement of a chemical from one location to another, or from one state (gas, liquid, solid) to another.

PCB—Polychlorinated biphenyl. An organic chemical often associated with electrical equipment such as capacitors and transformers.

Persistence—Ability to remain in the environment after long periods of time.

Pesticide—Generic name for any chemical that kills or deters a pest, including plants and animals.

Picloram—The active ingredient in several herbicide products registered for use on rights of way, fallow cropland or pasture (for example, Grazon and Tordon).

Polymeric—Term describing large molecules resulting from repeating molecules chemically bonded into large chains of varying lengths and degrees of branching. Many synthetic chemicals such as plastics are polymers.

Pores—Pockets of air of varying size within compost and soils. Bulking agents such as wood chips are often added to feedstock to increase the pore space, and thus the air content in the compost. Increased air content allows for greater microbial activity.

Recalcitrant—Not easily broken down in nature.

Structure—The shape of an organic molecule is its structure. Each organic chemical is made up of a number of building blocks that constitute a molecule when fully assembled. Each organic molecule must contain carbon and may contain any number of the following most commonly found atoms: hydrogen, oxygen, nitrogen, sulfur, and phosphorus.

TCE—Trichloroethene. An organic chemical that served as a solvent in the dry-cleaning industry and for cleaning (usually military) aircraft.

Thermophilic—Temperature range over 105°F.

Transformation—Chemical change ranging from minor to complete destruction.

Water solubility—Amount of a chemical dissolved in water.

Xenobiotic—Any synthetic chemical; literally meaning “foreign to life.”

Principal Authors

Andrew Singer, Lecturer, Department of Environmental Sciences, University of California, Riverside

David Crohn, Associate Professor, Department of Environmental Sciences, University of California, Riverside

Note: This fact sheet is intended to provide general information and point out issues to consider regarding composting. Reference does not imply endorsement by the California Integrated Waste Management Board. Updated in 2001 by CIWMB staff to include information on clopyralid and picloram. CIWMB staff can be reached at (916) 341-6620.

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, Flex Your Power and visit www.consumerenergycenter.org/flex/index.html.